

Supplemental Information for the
Endangered Species Impacts Assessment for the
ExxonMobil Oil Corporation - Joliet Refinery
Unit Reliability - Efficiency Improvement Projects

Prepared by:



September 20, 2005

This supplemental information is being provided to the United States Environmental Protection Agency (USEPA) and United States Fish & Wildlife Service (USFWS) as follow-up to the September 16, 2005 teleconference regarding the consultation being conducted for the Crude/Coker Utilization Project (CCUP), as required by Section 7 of the Endangered Species Act of 1973, as amended.

In the original report, "Endangered Species Impacts Assessment, ExxonMobil Oil Corporation - Joliet Refinery, Unit Reliability - Efficiency Improvement Projects" (prepared by ExxonMobil, dated August 3, 2005), worst case (most conservative assumptions, highest modeled receptor location) maximum N₂ deposition was modeled at 0.083 g/m²-yr, which is about 11% of 2003 background levels (0.70 g/m²-yr). During the September 16, 2005 conference call, the following items were discussed:

- Specific areas of model conservativeness (i.e., overprediction of impacts);
- Areas of emission inventory conservativeness (i.e., overprediction of emission rates);
- "Pre-mitigating" measures for the CCUP project that result from compliance with provisions of the Clean Air Act; and
- Clean Air Act regulatory developments that will further decrease background deposition levels in the near future.

As discussed in the September 16, 2005 teleconference call, ExxonMobil is to use in this supplement a ledger approach to account for other factors that can be used to predict a more realistic, yet still conservative estimate of impacts to N₂ deposition at the receptor locations. USFWS has requested quantification, wherever possible, of impacts.

Calpuff Model

As noted in the August 3, 2005 report¹, Indeck-Elwood Energy utilized Calpuff rather than ISCST3 to model N₂ deposition. Calpuff is a newer, better equipped model for estimating deposition rates for reasons noted in the Indeck-Elwood report² and the attached Cambridge Environmental memorandum on model comparisons (Attachment A to this report). Epsilon Associates has conducted Calpuff modeling of total (wet plus dry) N₂ deposition for the ExxonMobil CCUP. Epsilon's report is provided as Attachment B of this report.

The Calpuff results are compared with those of ISCST3 in Table 1. For the same receptor locations, the modeled impacts are one to two orders of magnitude lower with Calpuff. For the same worst case conditions used for ISCST3 modeling, the Calpuff-modeled impact on N₂ deposition is at or below 0.0015 g/m²-yr for all receptor locations.

Using the same model as was employed for the Indeck-Elwood Energy ESA consultation, modeled impacts on N₂ deposition are even lower than those of Indeck, for which USEPA and USFWS concluded incremental additions are "significantly below existing background rates and therefore any effect would not be measurable"³.

Emission Inventory Conservativeness, CCUP Projected Future Actual vs. Future Potential

As noted on Page 5 and Table 2 of the June 15, 2005 submittal "Draft Endangered Species Act Assessment, ExxonMobil Oil Corporation - Joliet Refinery, Unit Reliability - Efficiency

¹ "Endangered Species Impacts Assessment, ExxonMobil Oil Corporation - Joliet Refinery, Unit Reliability - Efficiency Improvement Projects", prepared by ExxonMobil, dated August 3, 2005. p. 34.

² "Ecological Risk Assessment for the Indeck Elwood Energy Center", prepared by Cambridge Environmental, Inc., April 2005, p. 4-1.

³ USEPA, Letter from Ms. Pamela Blakley to Mr. John Rogner of USFWS, June 7, 2005, page 8.

Improvement Project", worst-case "future potential" emissions under the Clean Air Act's Prevention of Significant Deterioration (PSD) program are based on allowable, potential emissions under the assumption of continuous operation 8,760 hours per year. ExxonMobil provided in Table 2 of the June 15, 2005 report anticipated future actual emissions. The actual emissions were estimated as 474.3 tons per year, which is 322.3 tons per year (or 40.4%) lower than the 796.61 tons per year associated with the CCUP permit.

Pre-Mitigating Measures for the CCUP Project

The September 12, 2005 ExxonMobil report "Supplemental Information for the Endangered Species Impacts Assessment for the ExxonMobil Oil Corporation - Joliet Refinery, Unit Reliability - Efficiency Improvements Project" provides information regarding the recent Coker Blowdown Recovery System (CBRS) that ExxonMobil has recently placed in service, and the project's impact on SO₂ emissions and resultant S deposition. Not only does this project provide for SO₂ emission reductions that are made federally enforceable in the CCUP permit, but also NO_x (and, as a result, N₂ deposition) reductions. The CBRS accounts for 219 tons per year of NO_x emission reductions, or 27.5% of the 796.61 tons per year associated with the CCUP. As demonstrated in the September 12, 2005 supplemental information report⁴, per ton deposition impacts resulting from CBRS emission reductions are equivalent to (or greater than) per ton increases from the CCUP. As ambient concentrations and depositions are directly proportional to emission rate, the anticipated reduction in modeled N₂ deposition is 27.5%.

As required by State Implementation Plan (SIP) provisions required by the Clean Air Act and found in 35 IAC 203, "Major Stationary Sources Construction and Modification (MSSCAM)", ExxonMobil is required to purchase NO_x and emission offsets from a qualifying source in the Chicagoland area airshed, the location shared by the site and all of the listed threatened and endangered species receptor locations for this analysis. Specifically, CCUP permit (currently proposed, permit not yet issued) condition 1.2.4 "Emission Offsets" requires 752.9 tons of NO_x emission offsets to be purchased and transferred from the source to ExxonMobil before startup of the modified operations covered by the CCUP permit.

A summer 2005 journal article⁵ details how the United States Department of Interior, National Park Service (NPS) recognized the validity of and allowed a source to use emission offsets as a mitigating measure for adverse impacts from S deposition in Class I areas. In addition, NPS was able to allow for offsets from one or more yet-to-be-determined sources from anywhere within an area much larger than the Chicago nonattainment area. Through complex modeling (using Calpuff), NPS allowed for emission offsets from 1:4 to 1:1, depending on the location of the offsetting source. 1:1 implies that reductions from the offsetting source would have an equivalent reducing impact on the habitat receptors as the location of the modifications. 1:4 implies that 4 tons of reductions at the offsetting location would be equivalent (from a deposition standpoint) to 1 ton of emissions from the location of the modifications. Assuming the same or better predictions for the smaller area covered by the Chicago nonattainment area, the 752.9 tons of NO_x emission offsets that ExxonMobil is required by CAA SIP provisions to obtain, would offset (reverse) the N₂ deposition increases from 188.22 to 752.9 tons of NO_x resulting from the CCUP permit action (23.6% to 94.5% of CCUP potential NO_x emissions increases).

⁴ Supplemental Information for the Endangered Species Impacts Assessment for the ExxonMobil Oil Corporation - Joliet Refinery, Unit Reliability - Efficiency Improvement Projects", prepared by ExxonMobil, September 12, 2005.

⁵ "Trading Places - An Innovative SO₂ Trading Program to Mitigate Potential Adverse Impacts on Class I Areas", two-part article in EM, Air and Waste Management Association, July 2005 (Part I - Impacts, pp. 30 - 35) and August 2005 (Part II - Mitigation Plan, pp. 28 - 32).

Future Clean Air Act Improvements to Background Levels of N₂ Deposition

On March 10, 2005 USEPA finalized the Clean Air Interstate Rule (CAIR), which calls for NO_x and SO₂ emission reductions of approximately 70% from baseline stationary source levels of 2003 for the eastern half of the United States (including the upwind states of Iowa and Missouri)⁶.

Assuming stationary sources account for half of all NO_x emissions, it is estimated that 35% of all NO_x emissions and, thus, N₂ deposition will be reduced. As a result, it is estimated that there will be a 35% reduction in background N₂ deposition levels from those of 2003 background. For the Bondville, Illinois monitor location that has been used for assessing the CCUP project impacts, this implies a reduction from 0.71 to 0.46 g/m²-yr (assuming deposition is directly proportional to ambient NO_x inventory).

Deposition Rate Corrected to Include Refinements Discussed Above

The following calculations show the refined net deposition rate resulting from the refinements discussed above.

Net Deposition = Background (1) + Indeck (2) + ExxonMobil Modifications (3)

(1) Background (adjusted⁷) = 0.46 g/m²-yr

(2) Indeck Highest Receptor Value (unadjusted) = 0.01 g/m²-yr

(3) ExxonMobil Highest Receptor Value (adjusted⁷) = $0.0015 \text{ g/m}^2\text{-yr} \times \{(796.6 - 322.3 - 219 - [188.2 \text{ to } 752.9])/796.6\}$
= $0.0015 \text{ g/m}^2\text{-yr} \times (0.0842 \text{ to } -0.625)$
= 0.000126 to -0.000937 g/m²-yr

Net deposition = (1) + (2) + (3)
= 0.46 + 0.01 + (0.000126 to -0.000937)
= 0.46906300 to 0.470126 g/m²-yr

As a result, with the current project considered under more realistic conditions (better model, anticipated actual emissions), adjustments for projects that have not been reflected in most recent background deposition (Indeck, ExxonMobil Coker Blowdown Recovery Project), and the consideration of the new CAIR Rule, total N₂ deposition rates will be about 33% lower than 2003 background. As a result, the project with all other considerations will have immeasurable effects and is less likely to adversely impact species diversity than 2003 baseline conditions.

6 C.V. Mathai, "CAIR/CAMR - Introduction to the Topic, EPA's Mercury & Pollutant Transport Rules, EM, Air & Waste Management Association, July 2005 issue, p. 8.

7 Assumes deposition is directly proportional to emission rate.

TABLE 1
COMPARISON OF CALPUFF AND ISCST3 MODEL RESULTS FOR NITROGEN DEPOSITION
CRUDE/COKE UTILIZATION -IMPROVEMENT PROJECT
EXXONMOBIL OIL CORPORATION - JOLIET REFINERY

HABITAT NAME	HABITAT LOCATION			ISCST3 MODEL RESULTS		CALPUFF MODEL RESULTS		COMPARISON
	UTM E	UTM N (km)	Distance from ExxonMobil Crude Unit Stack	ISCST3-Modeled Impact of ExxonMobil CCUP on Soil N Deposition Rate	ISCST3-Modeled Increase in Soil N Deposition Rate over Published 2003 Background	Calpuff-Modeled Impact of ExxonMobil CCUP on Soil N Deposition Rate	Calpuff-Modeled Increase in Soil N Deposition Rate over Published 2003 Background	Reduction by Employing Calpuff
	[km]	[km]	[km]	[g/m ² -yr]	%	[g/m ² -yr]	%	%
Footnote(s)			1	2	3	4	3	5
Grant Creek Prairie Preserve	400.5	4580.1	5.00	2.0E-02	2.85%	1.5E-03	0.21%	92.7%
Drummond Dolomite Prairie (XOM#1)	401.6	4583.9	1.32	7.0E-02	9.92%	8.2E-04	0.12%	98.8%
Drummond Dolomite Prairie (XOM#2)	401.7	4584.2	1.13	8.3E-02	11.74%	5.1E-04	0.07%	99.4%
Drummond Dolomite Prairie (USFW - MNTP)	401.7	4584.6	0.86	7.5E-02	10.62%	7.2E-04	0.10%	99.0%
Fraction Run	411.7	4603.0	20.85	3.0E-03	0.43%	1.4E-03	0.20%	53.4%
Dellwood Park Prairie	410.8	4603.5	20.85	3.7E-03	0.52%	1.4E-03	0.20%	62.0%
Lockport Prairie #1	410.2	4603.8	20.84	3.7E-03	0.52%	1.4E-03	0.20%	62.6%
Lockport Prairie #2	410.0	4603.8	20.77	3.7E-03	0.52%	1.4E-03	0.20%	62.8%
Lockport Prairie #3	410.0	4604.0	21.00	3.7E-03	0.52%	1.4E-03	0.19%	63.3%
Lockport Prairie #4	410.4	4604.6	21.71	3.7E-03	0.52%	1.3E-03	0.19%	64.6%
Material Services Corporation River South	410.7	4606.4	23.46	3.7E-03	0.52%	1.2E-03	0.17%	68.3%
Long Run Seep Nature Preserve	412.5	4608.7	26.26	2.4E-03	0.34%	1.0E-03	0.15%	56.4%
Romeoville Prairie Nature Preserve	410.6	4610.7	27.36	3.0E-03	0.43%	9.1E-04	0.13%	69.6%
Keepataw Preserve	413.6	4614.3	31.80	1.8E-03	0.26%	7.7E-04	0.11%	57.4%

¹Crude Unit Stack UTM coordinates are 401.01E (km) and 4585.07N (km).

²ISCST3 modeling conducted by ExxonMobil Research & Engineering, maximum total deposition rate calculated as 2X maximum modeled wet deposition (highest one-year average CCUP modeled impact from 5 years of meteorological data, 1986 to 1990).

³Background N deposition rate from Bondville, IL NADP data, 0.70552 g/m²-yr.

⁴Calpuff modeling conducted by Epsilon Associates, maximum total deposition rate calculated as sum of wet and dry N flux from NO_x, HNO₃, NO₃ (highest one-year average from five years of meteorological data, 1986 to 1990).

⁵Calculated by the equation X = [1 - (Calpuff Impact / ISCST3 Impact)*100], expressed as a percentage.

ATTACHMENT A

Cambridge Environmental Memorandum Regarding Calpuff vs.
ISCST3 Appropriateness for Deposition Modeling
September 19, 2005

MEMORANDUM

To: Brad Sims
From: Steve Zemba
Subject: ISCST3 v CALPUFF modeling for nitrogen deposition
Date: September 20, 2005

I write in follow-up to Friday's conference call (9/16/05) to detail the reasons why the CALPUFF model is better suited to predict nitrogen deposition than the ISCST3 model. I first, however, wish to note that the ISCST3-generated nitrogen deposition estimates provided in your August 3, 2005 report are overestimates of long-term averages because they are based on the highest modeled annual deposition estimate for any of the five years. If the five annual deposition values are first averaged at each receptor, the highest five-year average deposition estimate is $0.044 \text{ g/m}^2\text{-yr}$ [at the Drummond Dolomite Prairie (USFW - MNTP) location], a value about 6.3% as large as the background nitrogen deposition rate of $0.71 \text{ g/m}^2\text{-yr}$. Thus, to the extent that decision-making is being shaped by the projected nitrogen deposition increment of 11.5%, the regulatory agencies should consider this lower increment of 6.3% as the more appropriate estimate of long-term deposition as generated by the ISCST3 model.

However, even with this correction, the current use of the ISCST3 model as a screening tool to calculate potential nitrogen deposition from emission of nitrogen oxides from ExxonMobil's Joliet Refinery will result in significant overestimates, especially at locations near the refinery. The ISCST3 modeling is based on the simple but erroneous assumption that all nitrogen oxide emissions can be removed by rainfall (and hence contribute to nitrogen deposition) as they are introduced to the atmosphere. However, to be removed by precipitation, nitrogen oxides (NO_x , emitted mostly as NO) must first be converted to nitrate forms (nitric acid, HNO_3 , or particulate-bound NO_3^-). The reactions to convert the non-depositing NO_x species to depositable forms of nitrate require time to take place, typically needing several hours to complete to a significant degree (NO, the principal form of NO_x emitted, requires at least two sequential reactions). Atmospheric chemistry is quite complex, as described in references such as Seinfeld (1986), though the concept of the required transformation of NO_x to nitrates prior to their removal by precipitation is well-established.

The question of the degree to which the ISCST3 modeling overestimates nitrogen deposition is difficult to answer, as NO_x transformation rates, like all chemical reactions, depend upon temperature, availability of reactants, competing reactions, and other factors that vary in both time and space. Seinfeld (1986) describes measurements of NO_x conversion rates. In Los Angeles, empirical NO_x -to-nitrate conversion rates ranged from 5–10% per hour, and in Boston ranged from 14–24% per hour. Thus, an hour after its release, the empirical data suggest that less than a quarter of the NO_x emitted from the refinery would be found in a depositable nitrate form, and these emissions would at that point be located a considerable distance from the

refinery (5 miles downwind at a typical wind speed of 5 mph). At distances closer to the refinery, even smaller percentages of NO_x will be converted to nitrate. Consequently, the current ISCST3 modeling that assumes 100% of NO_x emissions are immediately converted to depositable nitrate upon release at the refinery leads to overestimates of nitrogen deposition at locations near the refinery – possibly by substantial margins.

The CALPUFF model is, in my opinion, a better model for estimating nitrogen deposition because it explicitly tracks both NO_x and nitrate species, and also contains simplified chemical mechanisms that model NO_x-to-nitrate conversion. The U.S. EPA does not recommend any models for estimating nitrogen deposition near an emission source of NO_x. In fact, most of its *Guideline on Air Quality Models* (Appendix W of 40 CFR Part 51) is devoted to recommending and differentiating models to estimate the atmospheric dispersion and dilution of pollutants in the atmosphere. The bulk of the Clean Air Act's provisions deal with pollutant concentrations in ambient air, and the deposition algorithms that have been added to models such as ISCST3 have been typically motivated by ancillary program concerns (such as interagency demands for conducting multi-pathway risk assessments of combustion source emissions). One notable exception is the requirement to estimate acid deposition impacts to federally-protected Class I airsheds (usually National Parks or wilderness areas) for which the CALPUFF model is the recommended approach.

Deposition algorithms have received little (if any) validation. Regulatory models such as ISCST3 have not been meaningfully evaluated with respect to their ability to match empirical deposition data (in contrast, the U.S. EPA has engaged in extensive monitoring studies that have yielded rich data sets to evaluate the performance of models to predict pollutant concentrations in ambient air). Hence, selection of the best model to predict nitrogen deposition must consider on theoretical grounds whether the relevant physical and chemical processes are considered. Both ISCST3 and CALPUFF are capable of modeling wet and dry deposition, but ISCST3 requires each chemical species to be modeled separately, and does not consider the time-dependent chemical reaction rates needed to transform emitted NO_x into depositable nitrates. Consequently, CALPUFF is the better model as it accounts for the appropriate first-order atmospheric chemistry that is needed to simulate NO_x transformation into the nitrate species that can be scavenged by precipitation.

Consequently, I believe the CALPUFF predictions of nitrogen deposition are more credible than those of the ISCST3 model (as currently implemented). Table 1 provides a comparison of the various nitrogen deposition estimates that have been generated thus far for the proposed ExxonMobil refinery project. The first deposition column reproduces the ISCST3-based estimates for the worst-case year from the August 3, 2005 report. The subsequent column provides five-year average estimates of nitrogen deposition, also constructed from the ISCST3 modeling approach, that serve as better estimates of long-term average deposition rates. These values are roughly a factor of two smaller than the worst-case annual estimates, but still probably

overestimate nitrogen deposition (especially at locations near the refinery) due to the instantaneous NO_x-to-nitrate conversion assumption. The third deposition column reproduces the nitrogen deposition estimates developed by scaling the CALPUFF modeling results for the Indeek facility (these values are also reproduced from the August 3, 2005 report).

The fourth deposition column entitled “ISCST3 adjusted with exponential conversion rate” represents a crude attempt to fix the erroneous instantaneous NO_x-to-nitrate conversion assumption in the ISCST3 modeling approach. The approach could be useful in cases in which ISCST3 modeling has already been developed and it is not practical to engage in detailed CALPUFF modeling. Assuming a linear NO_x-to-nitrate conversion rate, the fraction f of NO_x converted to nitrate at any given distance from the refinery is approximated by an exponential function of the form:

$$f = 1 - e^{-rx}$$

Based on a typical wind speed of 5 mph and an assumed conversion rate of 15% in one hour, the resulting value of r is 0.0105 km⁻¹ (see Appendix 1 for a detailed description of this derivation). Calculating the factor f for the location-specific distances from the refinery (as provided in the second column of Table 1) and multiplying by the five-year average ISCST3 modeling results in the ISCST3 adjusted nitrogen deposition estimates provided in the fourth deposition column. Finally, the last column of Table 1 provides the nitrogen deposition estimates for the facility-specific CALPUFF modeling that was recently completed for the ExxonMobil refinery. These facility-specific results represent the best available estimates of nitrogen deposition. The highest modeled nitrogen deposition rate of 0.00133 g/m²-yr represents a projected increment of 0.2% to the background nitrogen deposition rate of 0.71 g/m²-yr.

Comparing the estimates of the final three columns in Table 1, the values tend to fall within about a factor of two of each other. Given the level of uncertainty involved in dispersion and deposition modeling, this level of agreement is encouraging, and suggests that, in some cases, ballpark nitrogen deposition estimates can be generated without the use of the CALPUFF model. In particular, since the ISCST3-adjusted estimates provide results similar to the CALPUFF estimates, a simple scaling/adjusting algorithm might provide useful screening-level estimates that build on the ISCST3 modeling developed for many permit applications. There are even more sophisticated techniques that could be used to adjust/scale ISCST3 deposition results, such as the approach outlined in Appendix 1 that separately considers the two forms of nitrate subject to precipitation scavenging.

Please write or call if I can be of further assistance, and thank you for the continued opportunity to work with you on this matter.



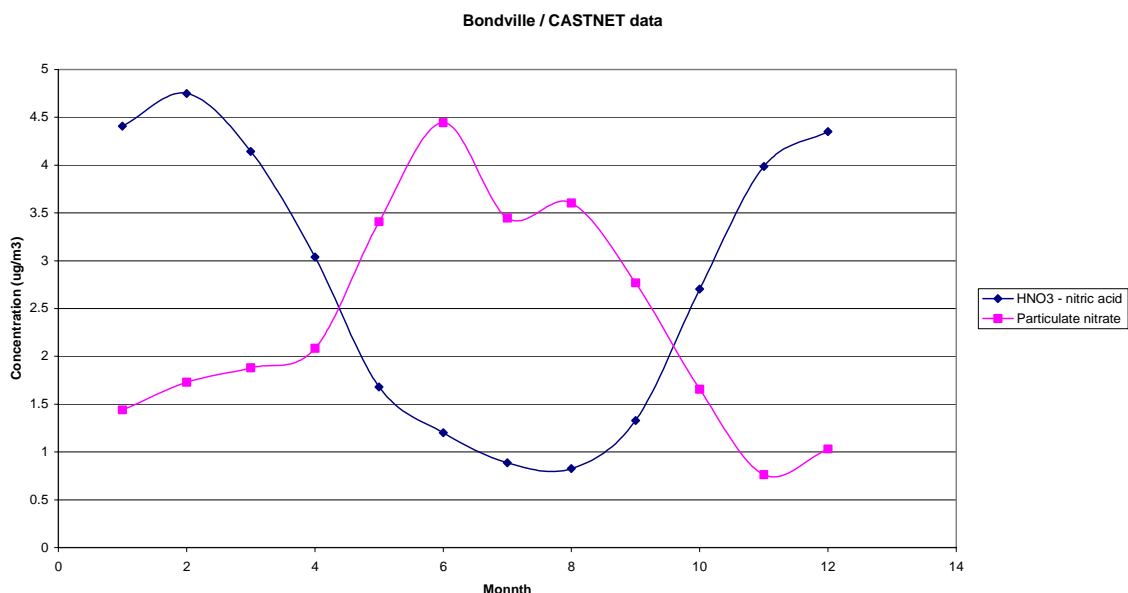
Table 1 Nitrogen deposition estimates constructed with various models and approaches

Species location	Distance from refinery (km)	Nitrogen deposition estimates (g/m ² -yr)				
		ISCST3 - worst-case year (as in August 03,2005 report)	ISCST3 - 5-year average	CALPUFF estimate scaled from Indeck (as in August 03,2005 report))	ISCST3 adjusted with exponential conversion rate	CALPUFF estimate modeled for ExxonMobil refinery
Grant Creek Prairie Preserve	5	0.02	0.012	0.00060	0.00060	0.00133
Drummond Dolomite Prairie (XOM#1)	1.32	0.07	0.037	0.00069	0.00051	0.00060
Drummond Dolomite Prairie (XOM#2)	1.13	0.083	0.037	0.00085	0.00044	0.00039
Drummond Dolomite Prairie (USFW - MNTP)	0.86	0.075	0.044		0.00040	0.00051
Fraction Run	20.85	0.003	0.002	0.00074	0.00039	0.00104
Dellwood Park Prairie	20.85	0.004	0.002	0.00087	0.00047	0.00102
Lockport Prairie #1	20.84	0.004	0.003	0.00066	0.00051	0.00098
Lockport Prairie #2	20.77	0.004	0.002	0.00067	0.00043	0.00096
Lockport Prairie #3	21	0.004	0.002		0.00040	0.00095
Lockport Prairie #4	21.71	0.004	0.002		0.00045	0.00092
Material Services Corporation River South	23.46	0.004	0.002		0.00044	0.00082
Long Run Seep Nature Preserve	26.26	0.002	0.001	0.00048	0.00034	0.00074
Romeoville Prairie Nature Preserve	27.36	0.003	0.001		0.00035	0.00067
Keepataw Preserve	31.8	0.002	0.001	0.00003	0.00028	0.00055

Appendix 1

Outline of a Better Method for Estimating Nitrogen Deposition with the ISCST3 Model

- Assume initially that all NO_x is emitted in the form of either nitric acid (HNO_3) or particulate nitrate.
- Model the NO_x plume with ISCST3 as if it were 100% HNO_3 or 100% NO_x (two separate runs)
 - For the 100% HNO_3 model the wet deposition with scavenging coefficients recommended in the CALPUFF model documentation ($\lambda = 0.00006$ for liquid precipitation, 0 for frozen precipitation). Estimate dry deposition post-model as the product of the ground-level concentration and an upper-end deposition velocity (3 cm/s is a representative estimate).
 - For the 100% particulate nitrate case, model small particle deposition with ISCST3 (both wet and dry, with appropriate scavenging coefficients for *e.g.*, 1 μm particles) and scale the results appropriately to NO_x emissions and an assumed particle form of ammonium nitrate.
- Use data from the CASTNET database to estimate the split between HNO_3 and particulate nitrate based on ambient data. This split varies seasonally (see plot below), which suggests that monthly deposition modeling should be considered.



- Adjust the deposition estimates based on the argument that in reality it takes time for the NO_x to convert through atmospheric reactions to HNO_3 and particulate nitrate. Empirical data and the CALPUFF model's MESOPUFF chemical mechanism can be used to support a typical to high-end conversion rate of 15% per hour. Using this value, and assuming an average wind speed of 5 m/s (example for now), the fraction f of converted NO_x is given by a growing exponential function:

$$f = 1 - e^{-rx}$$

where r (for this example) is 0.0105 km^{-1} . This value produces the following scaling factors:

Distance from source (km)	Fraction f converted
0.1	0.01
0.2	0.02
0.5	0.05
1	0.10
2	0.19
3	0.27
5	0.41
10	0.65
20	0.88
30	0.96

ATTACHMENT B

Calpuff Modeling Report, Epsilon Associates
September 1, 2005

MEMORANDUM

Date: September 1, 2005

To: Steve Zemba, Cambridge Environmental

Cc: Brad Sims, ExxonMobil

From: Liz Hendrick, CCM

Subject: **ExxonMobil CALPUFF Modeling for Nitrogen Deposition**

Cambridge Environmental retained Epsilon Associates to conduct CALPUFF modeling to assess nitrogen deposition from emissions from the ExxonMobil Joliet Refinery.

Modeling Description

- CALPUFF dispersion/deposition model and POSTUTIL and CALPOST postprocessors were used to evaluate the nitrogen deposition impacts.
- CALPUFF was run in single meteorological station mode.
- CALPUFF included chemical transformations of oxides of nitrogen (NO_x) to nitrate (NO_3) and nitric acid (HNO_3).
- Compute wet and dry deposition fluxes.
- POSTUTIL was used to extract the elements of nitrogen out of the compounds in the flux files and to combine wet and dry flux impacts.
- CALPOST was used to display the CALPUFF model deposition values for total nitrogen.

Model Inputs

- Source parameters provided by ExxonMobil for two operating scenarios, i.e., maximum future emission and past actual emission cases.

- Fourteen discrete receptors representing the areas of threatened/endangered species in the vicinity of the refinery were provided by ExxonMobil.
- Five years (1986-1990) of processed meteorological data in extended ISCST3 format (with additional parameters necessary for deposition modeling) were also provided by ExxonMobil. The data consisted of hourly surface observations collected by the National Weather Service (NWS) at O'Hare International Airport in Chicago, IL in conjunction with upper air data from Peoria, IL.

Model options

The CALPUFF model options corresponding to those specified in the IWAQM Phase 2 document as defaults were specified. The following options in CALPUFF were employed:

- Gaussian vertical distribution used in the near field
- Partial plume path adjustment
- Transitional plume rise computed
- Model stack tip downwash
- Use MESOPUFF II chemical transformation mechanism
- Model wet removal
- Model dry deposition
- Use PG dispersion coefficients for rural areas
- Do not adjust sigma y and sigma z for roughness
- Allow partial plume penetration of elevated inversions
- Horizontal size of puff (550 meters) beyond which time-dependent dispersion equations are used to determine sigma y and sigma z (Heffter equations)
- A 50 km by 50 km CALPUFF modeling domain was specified which encompassed the source and the sensitive receptors and incorporated a buffer zone beyond the receptors to allow for the recirculation of puffs beyond the receptors. A grid spacing of 1 km was specified.
- Conservative default background concentration for ozone of 80 ppb and default value for ammonia of 10 ppb were used.
- Gaseous phase dry deposition was modeled for NO_x , HNO_3 ; particle deposition was assumed for NO_3 .

Model post-processing

- POSTUTIL and CALPOST used to combine the wet and dry flux impacts and to convert flux units from g/m²/s of pollutant deposition to kg/ha/yr of nitrogen deposition. Deposition values for each of the oxides of nitrogen were adjusted for the difference between the molecular weight of the oxide and the element. The nitrogen contribution from each compound was summed to yield a total deposition value. The table below contains the multipliers used to correct for molecular weight differences and unit conversions for each pollutant.

	Multiplier in POSTUTIL	Multiplier in CALPOST (# of Hours)
S from SO ₂ flux	1.8 x 10 ⁴	8760 or 8784
S from SO ₄ flux	1.2 x 10 ⁴	8760 or 8784
N from NO _x flux	1.09562 x 10 ⁴	8760 or 8784
N from HNO ₃ flux	8.0 x 10 ⁶	8760 or 8784
N from NO ₃ flux	8.129032 x 10 ³	8760 or 8784
N from NH ₃ flux	2.9647 x 10 ⁴	8760 or 8784

Deposition model results

The results of the CALPUFF deposition model analysis are summarized in the table below. The table provides incremental predicted deposition rates for nitrogen at each sensitive receptor location (maximum future – past actual) for each year and the 5-year average. The highest nitrogen deposition, 0.0133 kg/hectare-year, is predicted to occur at Receptor #1, and represents a 0.19% increase over the background nitrogen deposition (7.0552 kg/ha-yr measured at Bondville, IL).

CALPUFF Total Nitrogen Deposition (kg/ha-yr)

Recp	UTM E (km)	UTM N (km)	1986	1987	1988	1989	1990	5yr avg	% Increase in N Dep
									over Bkgrd
1	400.481	4580.100	1.39E-02	1.33E-02	1.41E-02	1.47E-02	1.07E-02	1.33E-02	0.19%
2	401.597	4583.887	5.03E-03	4.85E-03	8.24E-03	7.14E-03	4.71E-03	5.99E-03	0.08%
3	401.709	4584.188	4.06E-03	1.66E-03	4.78E-03	5.13E-03	3.71E-03	3.87E-03	0.05%
4	401.729	4584.605	6.32E-03	4.75E-03	7.17E-03	3.27E-03	3.96E-03	5.09E-03	0.07%
5	411.709	4602.968	1.10E-02	1.01E-02	9.19E-03	7.72E-03	1.40E-02	1.04E-02	0.15%
6	410.818	4603.467	1.12E-02	9.64E-03	8.88E-03	7.18E-03	1.41E-02	1.02E-02	0.14%
7	410.212	4603.771	1.07E-02	8.91E-03	8.44E-03	6.91E-03	1.38E-02	9.75E-03	0.14%
8	409.992	4603.796	1.05E-02	8.70E-03	8.36E-03	6.89E-03	1.38E-02	9.65E-03	0.14%
9	410.049	4604.030	1.04E-02	8.53E-03	8.23E-03	6.80E-03	1.36E-02	9.50E-03	0.13%
10	410.415	4604.635	1.01E-02	8.27E-03	7.93E-03	6.57E-03	1.31E-02	9.19E-03	0.13%
11	410.734	4606.417	8.94E-03	7.13E-03	7.08E-03	6.02E-03	1.17E-02	8.18E-03	0.12%
12	412.543	4608.661	8.26E-03	6.62E-03	6.25E-03	5.36E-03	1.05E-02	7.39E-03	0.10%
13	410.597	4610.692	7.43E-03	5.47E-03	6.09E-03	5.35E-03	9.11E-03	6.69E-03	0.09%
14	413.565	4614.292	6.18E-03	4.51E-03	4.73E-03	4.28E-03	7.67E-03	5.48E-03	0.08%